

## Photoluminescence studies of SiC nanocrystals embedded in a SiO<sub>2</sub> matrix

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### Abstract

The dependence of the photoluminescence (PL) from SiC nanocrystals embedded in a SiO<sub>2</sub> matrix on annealing is presented. Blue-green PL has been observed at room temperature from annealed SiC–SiO<sub>2</sub> composite films. The intensity of the single emission band at 460 nm (2.7 eV) shows a strong dependence on the annealing temperature. The combination of high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared (FTIR) transmission spectra and PL results suggest that SiC nanocrystals have been incorporated into the SiO<sub>2</sub> matrix and O-deficient defects were formed. The origin of luminescence is attributed to the creation of defects in silicon oxide. © 2001 Elsevier Science B.V. All rights reserved.

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Recently, the luminescence properties and nonlinear optical behavior of Ge, Si, and C nanocrystals in silicon dioxide at room temperature have received considerable attention [1–6]. Several models have been suggested in attempts to clarify the origins of the luminescence properties of indirect-gap group-IV semiconductor nanocrystals [7]. Some researchers explain their results using a three-dimension quantum confinement model [1,2], while others believe that interface defects and emitting centers are responsible for PL emission [3–6]. However, the mechanism of group-IV semiconductor nanocrystals embedded in a SiO<sub>2</sub> matrix has not been determined conclusively. To test the validity of the models, one must make

systematic measurements of PL, crystal size, and surface (or interface) defect states of different group-IV semiconductor nanocrystals in a SiO<sub>2</sub> matrix. In our previous work, we performed detailed studies on the PL properties of germanium [5], silicon [6] and carbon [5] nanocrystals embedded in a SiO<sub>2</sub> matrix. The model of the luminescence centers is believed to explain the origin of PL emission for these samples.

Silicon carbide has attracted much interest as a semiconductor because of its potential in electronic devices and its important applications for high-temperature mechanical devices. The band-gap energy of SiC is considerably higher than that of silicon and varies with the polytype modification giving 2.3, 3.0, and 3.2 eV for the main polytypes, 3C, 6H, and 4H, respectively. In this Letter, we report the formation and luminescence properties of SiC nanocrystals embedded in a SiO<sub>2</sub>

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matrix. These samples were characterized by high-resolution transmission electron microscopy (HRTEM), Fourier transform infrared (FTIR) spectroscopy, and photoluminescence (PL). The results suggest that the SiC nanocrystals were incorporated into the SiO<sub>2</sub> matrix, and O-deficient defects were formed. Blue-green luminescence resulted from the creation of defects in silicon oxides. A strong dependence of PL on annealing temperature was observed. A model is proposed to explain the mechanism of these phenomena.

SiC–SiO<sub>2</sub> composite films were deposited on Si(1 0 0) wafers by RF co-sputtering SiC and SiO<sub>2</sub> targets [8,9]. Post-annealing treatment was performed between 400 and 1200°C in vacuum for 30 min to form SiC nanoparticles confined in a SiO<sub>2</sub> matrix. HRTEM was used to determine the structural properties of the SiC–SiO<sub>2</sub> composite films. PL spectra were measured under 325 nm (3.82 eV) excitation (He–Cd laser). All PL spectra were carried out at RT and corrected for the spectral response of the instrument. The overall temporal resolution of the photon counting system was approximately 100 ps, and the power density of the excitation beams was kept at 10 mW/cm<sup>2</sup>. FTIR transmission spectra were measured using a Perkin–Elmer 2000 spectrometer in the mid-IR region with a resolution of 4 cm<sup>−1</sup>.

The as-deposited SiC–SiO<sub>2</sub> composite films were amorphous, while nanocrystals were observed in annealed samples. Typically, SiC nanocrystals of about 5 nm in diameter have been observed in the 740°C annealed samples using HRTEM.

The PL spectra of these SiC–SiO<sub>2</sub> composite films were measured under 3.82 eV (325 nm) photoexcitation, and a typical spectrum after annealing at 950°C is shown as an inset in Fig. 1. This PL spectrum shows a single peak at 460 nm (2.7 eV), which is similar to those observed in Si and C nanocrystals in SiO<sub>2</sub> [5,6].

The origin of the PL for SiC–SiO<sub>2</sub> could be due to two possible reasons: (a) SiC nanoclusters with small diameters; or (b) triplet-to-ground transitions of neutral oxygen vacancies in silicon oxide, or Si–O related emitting centers. In (a), the PL is attributed to the quantum confinement effect. In low-dimension systems, PL emission is thought to

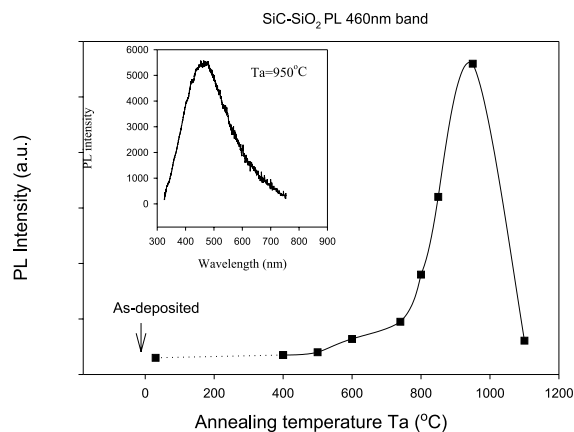


Fig. 1. PL intensity at 460 nm (2.7 eV) of SiC–SiO<sub>2</sub> composite films under 325 nm excitation as a function of the annealing temperature. (All samples were annealed in vacuum for 30 min). The inset shows the PL spectra of SiC–SiO<sub>2</sub> films after annealing at 950°C.

correlate with the radiative recombination of excitons confined in the nanocrystals. The exciton Bohr radius can be expressed as

$$a_B = \epsilon \hbar^2 / 4\pi^2 \mu e^2,$$

where  $\hbar$  is the Planck constant,  $\epsilon$  is the static dielectric constant,  $\mu$  is the reduced mass for excitons ( $1/\mu = 1/m_h^* + 1/m_e^*$ ,  $m_h^*$  and  $m_e^*$  are effective masses for holes and electrons, respectively), and  $e$  is the electron charge. For the group-IV semiconductors in strong quantum confinement,  $a_B \sim 4\text{--}20$  nm. This value is comparable with the crystal size determined from HRTEM. Several researchers use this model to explain the photoluminescent properties of nanocrystallite Ge embedded in a glassy SiO<sub>2</sub> matrix [2], and Si and Ge quantum dots [1]. We note that the basic experimental phenomenon in their studies was the existence of a photoluminescence blueshift when the nanocrystal Si (or Ge) size was reduced [1,2,10]. However, in our experiments, only a single peak at 460 nm (2.7 eV) was observed in all our SiC–SiO<sub>2</sub> samples; no shift of PL peak position was observed with increasing annealing temperature. Similar results (no shift of PL peak energy positions) were also observed for Ge and C nanocrystals embedded in a SiO<sub>2</sub> matrix [5]. We therefore find it difficult to explain the PL properties of SiC, Ge and

C nanocrystals embedded in a  $\text{SiO}_2$  matrix using the quantum confinement model.

To examine if interface defect models are viable models to explain the origin of PL from SiC nanocrystals embedded in a  $\text{SiO}_2$  matrix, we next turn to our FTIR data. FTIR transmission spectra of as-deposited and annealed SiC– $\text{SiO}_2$  composite films are shown in Fig. 2. FTIR measurements showed SiC absorption at  $803\text{ cm}^{-1}$  and the Si–O stretching absorption band at  $1030\text{ cm}^{-1}$  for the as-deposited film [11]. Increasing the annealing temperature from  $300^\circ\text{C}$  to  $1000^\circ\text{C}$  caused a shift in the absorption bands (to higher wave number) and a broadening of the  $\text{SiO}_2$  absorption peak. Fig. 2 shows that the SiC absorption shifted to  $816\text{ cm}^{-1}$  and the  $\text{SiO}_2$  absorption to  $1055\text{ cm}^{-1}$  after the films were annealed at  $740^\circ\text{C}$  in vacuum for 30 min. Both SiC and  $\text{SiO}_2$  absorption peaks were shifted to higher wave numbers by 13 and  $25\text{ cm}^{-1}$ , respectively. Furthermore, the intensity of SiC absorption relative to that of the  $\text{SiO}_2$  increased by more than a factor of two after annealing at  $800^\circ\text{C}$ , corresponding to the aggregation of SiC nanocrystals from the amorphous SiC phase. The formation of SiC nanoparticles after annealing to higher temperature also results in increased strain. On the other hand, the  $\text{SiO}_2$  absorption peak broadened and a shoulder (on the higher wave number side) became obvious for films annealed to  $740^\circ\text{C}$  and higher. This shoulder is similar to that observed in nanocrystalline carbon in a  $\text{SiO}_2$  matrix [5]. One possible explanation is that the shoulder could be due to absorption by O-deficient defects at the SiC/ $\text{SiO}_2$  interface, which are created after annealing. This observed modification of lineshape of the Si–O stretching band at  $1055\text{ cm}^{-1}$  due to thermal treatment is consistent with that observed when the O/Si ratio at the Si– $\text{SiO}_2$  interface increases during the oxidation of single crystal Si surfaces [12,13].

The PL intensity of SiC– $\text{SiO}_2$  composite films as a function of annealing temperature is shown in Fig. 1. The PL intensity increases with increasing annealing temperature, and after reaching a maximum, it decreases at higher annealing temperatures. The optimized annealing temperature was found to be about  $950^\circ\text{C}$ .

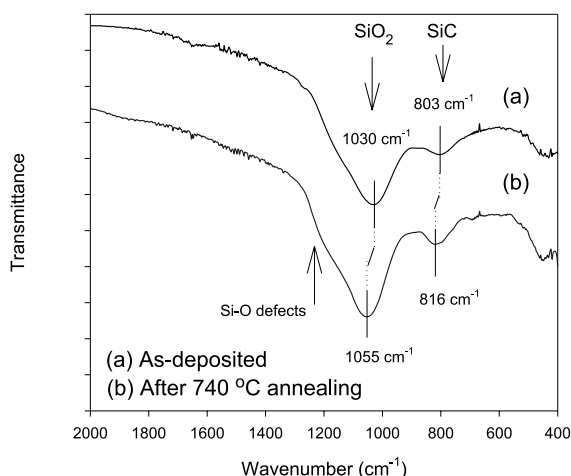


Fig. 2. FTIR spectra of (a) as-deposited and (b) annealed SiC– $\text{SiO}_2$  composite films. Increasing the annealing temperature caused a shift of the absorption bands and a broadening of the  $\text{SiO}_2$  absorption peak.

From our HRTEM, FTIR and PL results, the origin of PL and the mechanism of dependence of PL on annealing temperature can be explained by the creation and thermal stability of luminescence centers as follows: The observed blue-green luminescence results from the creation of defects in silicon oxides. These defects (e.g., twofold-coordinated silicon such as  $-\text{O}-\text{Si}-\text{O}-$  and  $-\text{O}-\text{Si}-\text{C}-\text{O}-$  and neutral oxygen vacancy defects) were formed mainly at the interface between SiC nanocrystals and the  $\text{SiO}_2$  matrix. The defects are believed to be the origin of emission (luminescence centers). The excitation takes place in the nanocrystals, where the excited conduction band electrons diffuse to the interface where the electrons interact with holes (emission centers) and result in radiative recombination. When the annealing temperature increases, the number and size of nanocrystals as well as the total surface area of nanocrystals increases. The local strain induced due to crystallization greatly facilitates the formation of Si–O related emitting centers. The intensity of PL therefore increases with increasing annealing temperature since the number of Si–O related emitting centers increases. This mechanism dominates before the annealing temperature ( $T_a$ )

reaches the optimized annealing temperature ( $T_a = 950^\circ\text{C}$ ). At higher annealing temperatures (beyond the temperature of thermal stability of luminescence centers), the number of luminescence centers decreases with increasing annealing temperature, resulting in a corresponding decrease of PL intensity.

In conclusion, SiC nanocrystals embedded in a SiO<sub>2</sub> matrix were prepared by annealing SiC–SiO<sub>2</sub> composite films. We have observed room-temperature PL near 2.7 eV in annealed SiC–SiO<sub>2</sub> composite films, and a strong dependence of PL intensity on annealing temperature. The origin of luminescence is suggested to be due to the creations of defects in silicon oxide at the SiC/SiO<sub>2</sub> interface.

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